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N91-19017

1990

NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA

CHARACTERIZATION OF THE CORROSION RESISTANCE OF SEVERAL ALLOYS TO
DILUTE BIOLOGICALLY ACTIVE SOLUTIONS

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Contract No:	NGT-01-002-099 The University of Alabama

ABSTRACT

Sulfate reducing bacteria (SRB) and acid producing bacteria/fungi detected in hygiene waters increased the corrosion rate (measured by resistance polarization) in Al 2219-T87. Furthermore, biologically active media enhanced the formation of pits on metal coupons. Direct observation of gas evolved at the corrosion sample, coupled with scanning electron microscopy and energy dispersive x-ray analysis of the corrosion products indicates that the corrosion rate is increased because the presence of bacteria favor the reduction of hydrogen as the cathodic reaction, instead of the production of (OH) - through the reaction of oxygen and water. SEM verifies the presence of microbes in a biofilm on the surface of corroding samples. The bacterial consortia are associated with anodic sites on the metal surface, aggressive pitting occurs adjacent to biofilms. Many pits are associated with triple points and inclusions in the aluminum alloy microstructure. Similar bacterial colonization was found on the stainless steel samples. Fourier Transform Infrared Spectroscopy (FTIR) confirmed the presence of carbonyl groups in pitted areas of samples exposed to biologically active waters.

OBJECTIVE

The objective of this project was to examine the corrosion resistance of several alloys (Aluminum 2219-T87 & AISI 316L Stainless Steel) to biologically active agents found in Environmental Control and Life Support System (ECLSS) waters. An attempt was made to correlate corrosive attack to the microstructure and compositions of the alloys examined, to the electrochemistry of the fluid media and to the microbial population of the ECLSS waters.

INTRODUCTION

The study of microbiologically influenced corrosion (MIC) is an interdisciplinary effort. An understanding of metallurgy, microbiology and electrochemistry is crucial to the resolution of MIC problems.

MIC is recognized as a major problem in many industries. The MIC problem is ubiquitous; most alloys, with the possible exception of titanium based alloys, are affected by MIC. The problem is particularly insidious because MIC can occur during system construction, during operation, or during shutdown periods. In fact, extended periods of shutdown can be particularly damaging. The stagnant water and other opportunity for the proliferation of micro-organisms. Researchers have developed an understanding of environments that promote MIC, materials susceptible to MIC, methods to detect damaging organism and

empirical approaches to the treatment and prevention of MIC. However, little understanding of the metallurgical bases for these processes has developed. Microbes attach to a variety of areas on the metal surface and form discrete deposits. In some cases these have been observed to form preferentially near weldments. Many researchers have examined the characteristics of micro-organisms as they relate to MIC. Few however, as a result of forming, welding or heat treating, has on their susceptibility to MIC. Microbes are living agents of corrosion. Their size (0.2u to 100u long, .2u to 5 u wide) provides them access to structural chemical and toward food, microbes often have specific receptors for target chemicals in their environment. Nutrients that may be scarce in flowing water are concentrated at metallic surfaces - Darwinism dictates that those microbes able to attach and establish themselves on metal surfaces will be at an advantage in such environments. Microbes can withstand wide temperature variation (-10 to 99 deg C), prolific and can exist in large colonies. Most microbes are able to form extra-cellular slime layers. This slime layer can also be involved in the formation of oxygen depletion cells, it can act as a sequestering agent for corrosion products and accelerate corrosion, and it can act as a barrier to biocide.

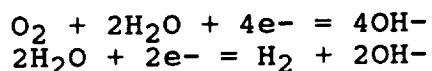
Many species of microbes produce a variety of organic acids, and enzymes that may influence the rate of corrosion. Hydrogenase, and metallic sulfides (product of SRB) have been reported to depolarize cathodic sites and accelerate corrosion. Some bacteria directly oxidize or reduce metallic ions. Carbon dioxide produced can become carbonic acid. The accretion of low solubility reaction products can lead to concentration cells. Microbes can form synergistic communities with other microbes or with higher life forms. These consortia can accomplish complex chemical reactions and can create aggressive environments. Organisms that produce organic acids under biofilms can lower local pH drastically. Any bacteria that contributes to the oxidation of metal ions will, at minimum, cause a passive co-accumulation of negative ions (e.g. Cl⁻). This may lead to the formation of acidic ferric chloride, cuprous chloride, magnesium chloride etc..solutions at crack tips, producing an in-vivo stress corrosion cracking environment more severe than many in-vitro tests. Slime layers produce a crevice like anaerobic environment in which passive films damaged by abrasion or by halide ion attack go unrepaired. The biofilm can consume oxygen, and prevents oxygen in the external environment from reaching the surface and restoring passive films; this work has shown that it may also promote cathodic reactions that do not involve oxygen.

SRBs can flourish in the anaerobic environment at the film metal interface, rendering the environment more chemically aggressive and providing several mechanisms to depolarize the rate limiting cathodic reaction. A catalogue

of microbes implicated in MIC of various alloy systems is provided in the literature.

Metal surfaces are extremely heterogeneous. Regional differences are so well defined that local anodes and cathodes form and corrosion can take place on individual pieces of metal. Surface condition, stress state, microstructure, chemistry and inclusion size and distribution affect local electrochemistry and MIC susceptibility. In many cases, welding seems to favor MIC. Welding changes the surface texture in the vicinity of the weld, produces local stress fields and causes other chemical, microstructural and mechanical changes that will affect the way microbes interact with the weld region.

Corrosion implies the existence of an anode, where oxidation of metallic atoms to soluble metallic ions takes place. Cathodic regions, where reduction takes place, balance the reaction. In systems where external current is not supplied, anodic and cathodic currents must be equal. Reactions at the anode and the cathode can be described as "half reactions", whose sum is the total corrosion reaction. Corrosion potentials are thermodynamic quantities, measured at equilibrium, and as such indicate what is possible. Corrosion currents are kinetic values, and reflect dynamic, nonequilibrium processes at electrodes. Typically there is one anodic reaction, however there may be several cathodic reactions; which is favored depends on the chemistry of the environment. In the system studied, pH was near neutral, and two cathodic reactions are probable:



In biologically active media other reactions are possible, including the reduction of metal ions themselves, or the reduction of sulfate.

When current flows in a corroding system, the potential difference between cathode and anode diminishes, this decrease is termed polarization. Polarization decreases the corrosion rate, and can occur at either anode or cathode. The phenomena can be caused by concentration effects - a necessary reactant is depleted at an interface, by activation effects - a crucial reaction step requires large activation energy (Tafel kinetics), or by ohmic effects - resistance at the interface slows the corrosion process. Many researchers ascribe MIC to depolarization accomplished by microbial agents. Some evidence for depolarization was found in this study.

MATERIALS AND PROCEDURES

Disks of Al 2219 and 316L stainless steel, 5/8" in diameter were degreased in trichloroethylene, and washed with ethanol to remove surface films. Disks were used for

polarization resistance studies in an EG&G 350A laboratory apparatus. These studies were extended over a three week period. The program POLCUR, as modified by Danford, was used to estimate Tafel Constants and calculate corrosion rates. A polarization resistance measurement is performed by scanning through a potential range very close to E_{corr}, large potential swings that damage the coupon surface are avoided. The corrosion current is related to the slope of the E-E_{corr}/ current plot at E-E_{corr} equal to zero through the Stern-Geary relationship:

$$I_{corr} = B_a B_c / [2.3 (B_a + B_c) R_p]$$

B_a, B_c are anodic and cathodic Tafel Slopes

Cells employed mild corrosive water, sterile corrosive water, and corrosive water with a 10,000 to 1 dilution of ECLSS waters as electrolytes. Disks were also exposed to the same media in erlenmeyer flasks, and examined by optical and scanning electron microscopy after fixing in formaldehyde. Optical microscopy for biological agents was accomplished by staining with acridine orange, and photographed using an epifluorescence microscope. Specimens for SEM were prepared by drying in absolute ethanol and freon, then sputtercoated with Au. Regions of these disks were examined with FTIR and EDAX.

RESULTS AND DISCUSSION

Figures 1 and 2 show I_{corr} over a three week period. Note that initial measurements are not enough to define the relationship that develops over longer periods. The 2219 exposed to sterile corrosive water corrodes at much lower rates than either the laboratory corrosive water or the ECLSS added media. In addition, few pits (2) were found on the sterile coupon when examined at 50X, limited localized buildup of hydroxide was noted, and limited gas evolution was observed. In contrast, the coupons exposed to biologically active media exhibited numerous pits, were covered with hydroxide mounds, and produced copious amounts of gas. Many pits formed adjacent to bacterial buildups. Bright, reduced surfaces were present under the buildup, as were additional pits. The corrosion rates of stainless steel in these same media are several orders of magnitude lower. Further, the stainless coupon exposed to sterile water corrodes most rapidly. MIC kits from BioIndustrial Technologies Inc. indicated the presence of SRB's and acid producers in ECLSS waters diluted 10,000 to 1 and used as test media in the EG&G 350A for five days. Minitek analysis of similar media strongly indicated the presence of several *Pseudomonas* bacteris (*paucimobilis* and *pickettii*) in the ECLSS added solutions. One species, *Moraxella* was found in sterile waters that had been used as a test media for five days. Biofilm development was evident on Al 2219 exposed to

ECLSS waters for one day, similar films were found on the stainless steel samples. Notice the relation between the nascent pit and the biomass. EDAX of similar pitted areas on samples exposed for a five day period showed high concentrations of sulfur, and CuAl_2 particles in relief. Reflectance FTIR spectra of samples exposed to ECLSS waters for five days was contrasted with samples exposed to sterile waters for the same period. Carboxyl groups were evident in the bioactive sample, indicating the presence of organic acids on the surface.

CONCLUSIONS

- 1) SRBs and acid producing bacteria are present in ECLSS waters.
- 2) MIC of Al 2219 was evident in the media studied.
- 3) Colonization of the 316L samples was evident.
- 4) Enhanced corrosion of Al 2219 is caused by promotion of the more rapid hydrogen evolution reaction at the cathode. This occurs because the bacteria metabolize oxygen near the interface and produce a film that fosters anaerobic conditions. In addition, the action of SRBs serves to favor this reaction.
- 5) The formation of sulfides and/or the presence of hydrogenase may serve to depolarize the cathodic reaction.
- 6) The presence of acid producing bacteria, in conjunction with the identification of carboxyl groups in FTIR of sample surfaces indicates that organic acids may aggravate corrosion in this system.
- 7) Microbes act as "catalysts" for corrosion, in a literal and in a figurative sense. They are adaptable, rapidly locate susceptible areas, locally fix anodes, accumulate corrosive chemical agents from their environment and produce corrosive metabolic end-products.

ACKNOWLEDGEMENTS

The list of people who deserve thanks reads like roll call at the M&P lab. Proceeding east to west, special thanks are due Dr. Merlin Danford, who had the unenviable task of "teaching teachers" this summer, but was always there with guidance, support, interest and Red Diamond. Thanks to Joe Montano who got me here, Barry "softball mogul" Moody, Carla Hooper, Wendell Deweese, Fred Gluszek, Jim Coston, Jeff Sanders and the rest of the Corrosion and Failure groups. The microbiology group in the western wing went out of their way to help and advise at every juncture. Special thanks are due to Dr. Elizabeth Rodgers, Gwinneth Smithers, Tim Huff and Don Ovenjuber. I hope that I have not "bugged" people too much this summer. Thanks to Mike

Freeman and Frank Six, without whom the program would not exist.

Figure 1

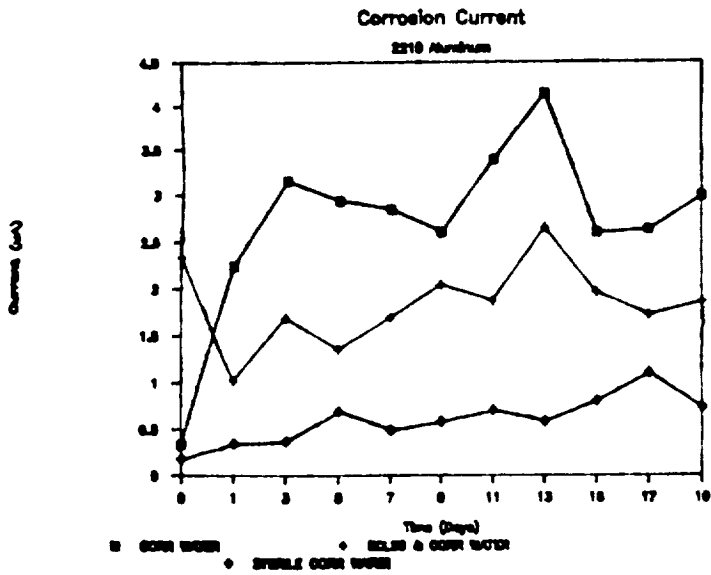
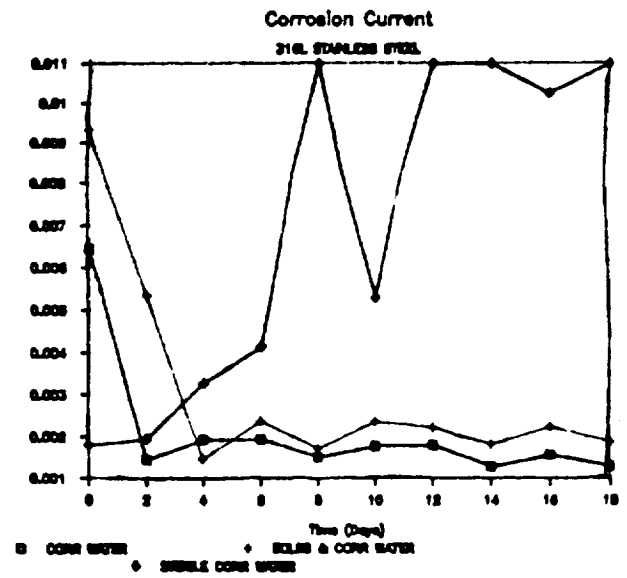


Figure 2



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